Cathodoluminescent Study of White Gangue Dolomites,
Jefferson City Mine, Mascot
Jefferson City District, Tennessee

Stuart Wolf

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Advisor:

Dr. D.E. Pride

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Introduction

The ability of the cathode ray to reveal or enhance structures and properties of minerals not visible in plane polarized light makes it a valuable petrographic tool. It has been known for some time (Sippel, 1965) that the method of cathodoluminescence, when applied to carbonates, can disclose overgrowth, cementation and zoning phenomena. The latter, if traceable from grain to grain, or ultimately from thin section to thin section, can provide a detailed history of the growth of the crystals. In this study, specimens from the Jefferson City Mine in the Mascot-Jefferson City mining district in Tennessee were examined with the hope of exposing just such a growth history. Previous cathode work done in the seventies in the mines to the southwest of the Jefferson City by Michael Ebers revealed a definite time correlative relationship in the deposition of sphalerite and dolomite in the open fractures of the brecciated country rock. The possibility of correlating his findings to the unexamined Jefferson City Mine is an interesting offshoot to the purpose of this paper.

Cathodoluminescence

The emission of nonthermal radiation (ultraviolet, visible, or infrared light) as a result of bombardment and excitation by a beam of electrons is referred to as cathodoluminescence. The term luminescence is associated with all light emission effects. Therefore, a more specific term for the phenomena should be adopted. In the last century, the physical science of light emission phenomena has grown to distinguish between two types of luminescence: fluorescence and phosphorescence. In fluorescence, the period of light emission is restricted to the time of excitation, and is due entirely to nonthermal causes. If light emission continues after the excitation is stopped, the phenomena is referred to as phosphorescence. In some cases, however, the production of a phosphorescence does not require the presence of any excitation, e.g., thermoluminescence. Since the luminescent properties observed in cathode work are limited to the time of electron bombardment of the specimen, and is largely unaffected by thermal influences, the method should properly be called "cathodofluorescence" (Sippel, 1965; Long and Agnell, 1965).

It is not within the scope of this paper to give a detailed theoretical description for the causes of luminescence, but a brief discussion of the physics behind the phenomena will be presented.

When impinging radiation is sufficient to excite an atom or molecule to the point of jumping to a higher energy level, fluorescence occurs. Under these conditions the input energy is entirely absorbed. By emitting radiation energy, in this case in the form of light, the excited atom or moledcule will change to its previous level of energy.

The energy quanta necessary to excite an atom of an element of distinct atomic number are equivalent to the emitted radiation energy in the recombining phase. This is illustrated by the equation:

$$E_{in} = h\nu = E_{out}$$

with h equal to Planck's constant and v equal to frequency. With increasing atomic number and nucleus charge of an element the energy must be increased to excite the atoms. This is so because in those atoms the bonding forces are much stronger due to the completion of the electron shells and the reduced atomic radii. The wavelength of emitted radiation always is longer than that of the exciting radiation. The energy quanta equation above shows a shifting of the emission spectra towards shorter wavelengths for elements with increasing atomic number. For the scope of the cathodoluminescence and its photographical reproduction, the emission ranges at both sides of the visible spectrum may be neglected (Zinkernagel, 1978).

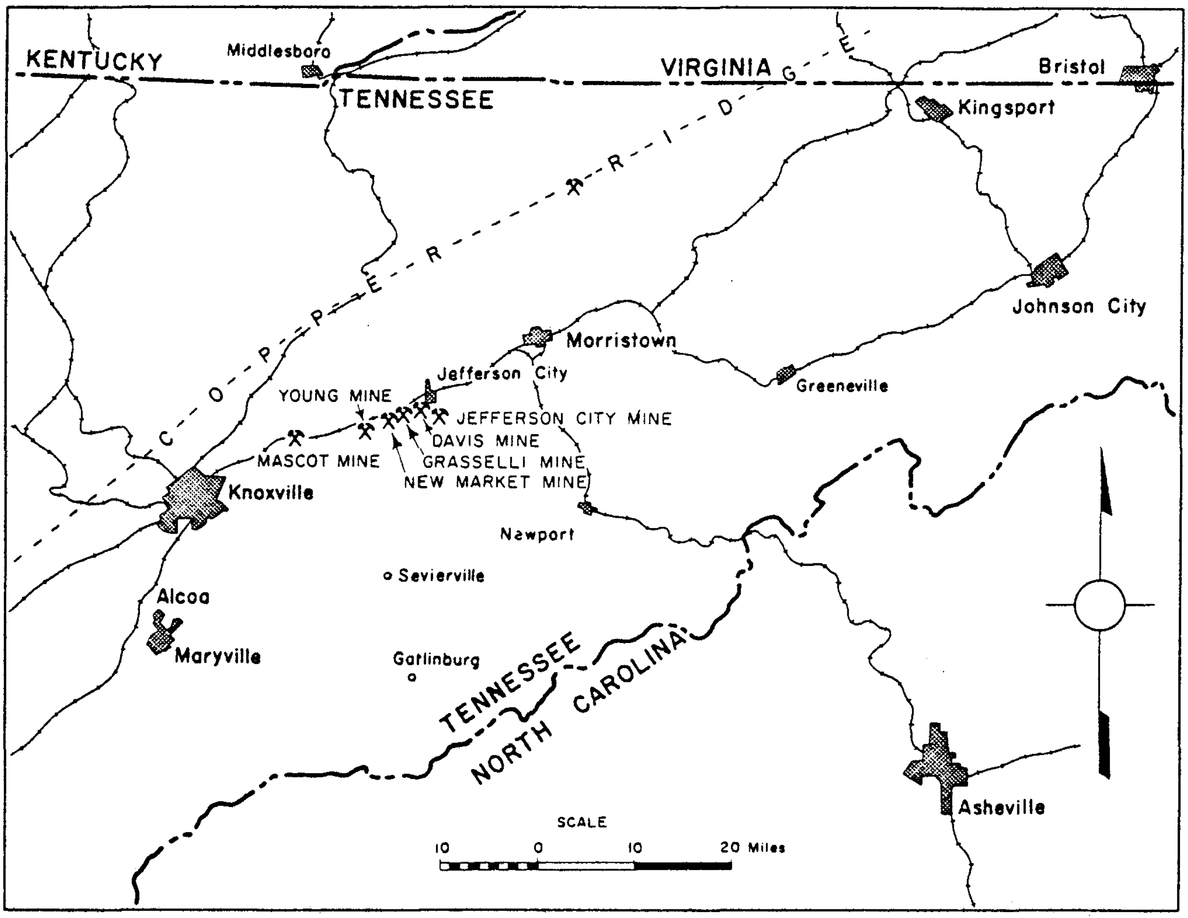
The Luminoscope

The gun used in this study is referred to as a cold cathode discharge tube. It functions on the principle of a low pressure environment enabling positive ions to acquire enough energy to release electrons from a high negative voltage surface. These electrons sustain the discharge by being accelerated by the high negative potential and the creation of more ions. If the pressure is too low, not enough gas molecules are available to be ionized and current is insignificant. If the pressure is too high the path length of the positive ions is too short for them to reach the energy required to release electrons from the cathode surface. When conditions are right, the electrons discharged from the cathode surface are accelerated towards the anode in a horizontal plane. A magnetic deflection system directs the beam down onto the specimen. The intensity of the luminescence that results from this electron bombardment is due to several factors. Among them are: the degree of light in the working area, the magnification of the ocular being used, and most importantly the surface density of the luminescent activators being exposed. Surprisingly, this instrument has proved superior to the electron microprobe for luminescence observations. One reason being that the luminescent features present may be compared more easily with structures visible in normal petrographic practice. Another advantage is that the preparation of the thin section is less involved; being that ordinary uncoated, unpolished thin sections may be used. The final advantage is that much larger areas of the specimen may be illuminated by the electron beam and viewed with low power objectives (Sippel, 1965).

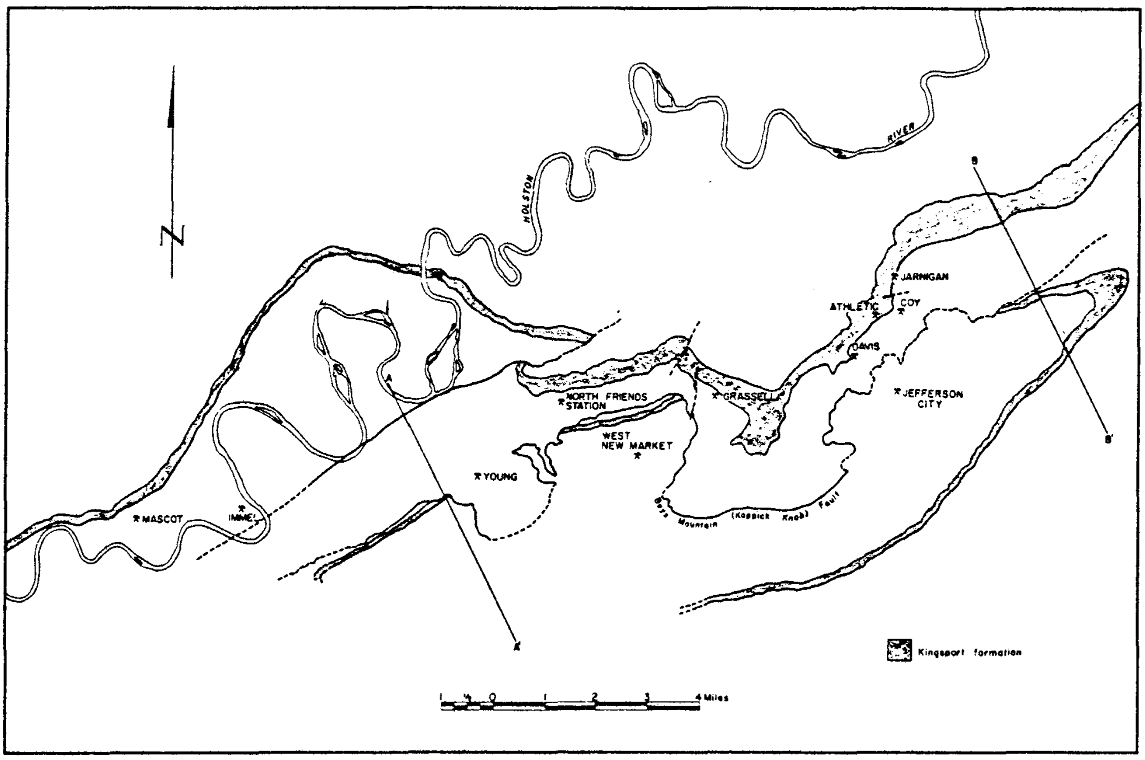
Topography and Structure

The samples for this study were taken from the New Jersey Zinc Company's Jefferson City Mine, which is located in the Mascot-Jefferson City district. This region is in the central part of the valley of Eastern Tennessee, part of the Appalachian Valley and Ridge Province. The mining district is bounded on the southeast by the Great Smokey Mountains and on the Northwest by the Cumberland Plateau. The topography of the district could be considered to be a subdued example of the valley and ridge type. Locally, it has been greatly modified by a highly developed karst system. Maximum relief in the district is between 1050 feet to 1500 feet above sea level, but slopes generally are quite gentle. Present topography is the result of almost continuous erosion of the Paleozoic sedimentary lithologies since the Appalachian orogeny.

The dominant structure of the valley is a series of subparallel sheets or belts of rock, thrust northwestward on southeast dipping faults that may be traced on strike for many miles. The structure of the belts is homoclinal, though in some places anticlines and synclines are formed. The Rocky Valley overthrust fault is one of the outstanding structural features, extending through the entire district. All of the known commercial ore bodies occur in the footwall of this fault.



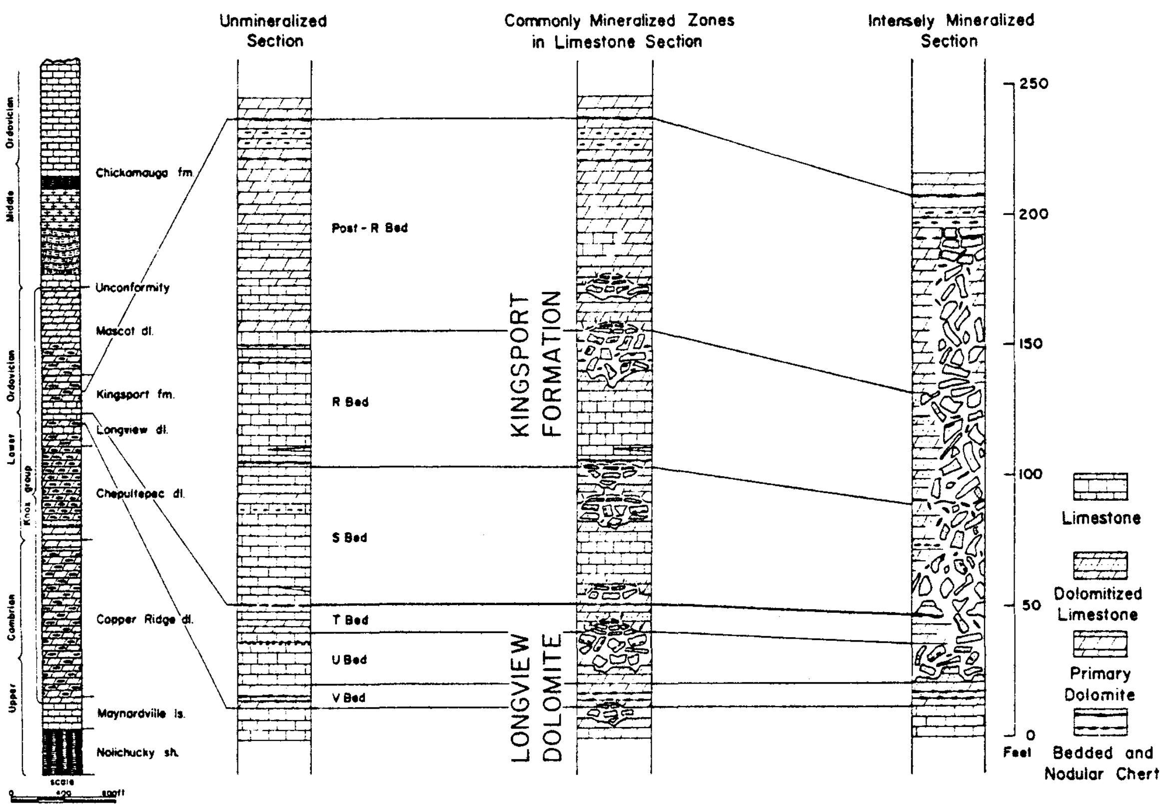
Map of Location of Mascot-Jefferson City
Zinc District, Tennessee



Map Showing Location of Mines
in the Mascot-Jefferson City Zinc District
and Relationship to Kinsport, Formation, Outcrop

Mineralogy and Lithology

The mineralogy at the Jefferson City mine is unusual in its simplicity. The only primary metallic mineral of economic significance being a pure sphalerite containing less than 0.5 percent iron. Minor amounts of pyrite, chalcopyrite, and galena have been found but are rare. The zinc ore in the Mascot-Jefferson City District is strata bound and occurs in the Lower Ordovician members of the Knox dolomite, Longview and lower Kingsport formations. The lithology of these formations consists of dense limestones interbedded with fine grained dolomites. Sandy zones and chert nodules occur at irregular intervals throughout this section and into the overlying Mascot dolomite.

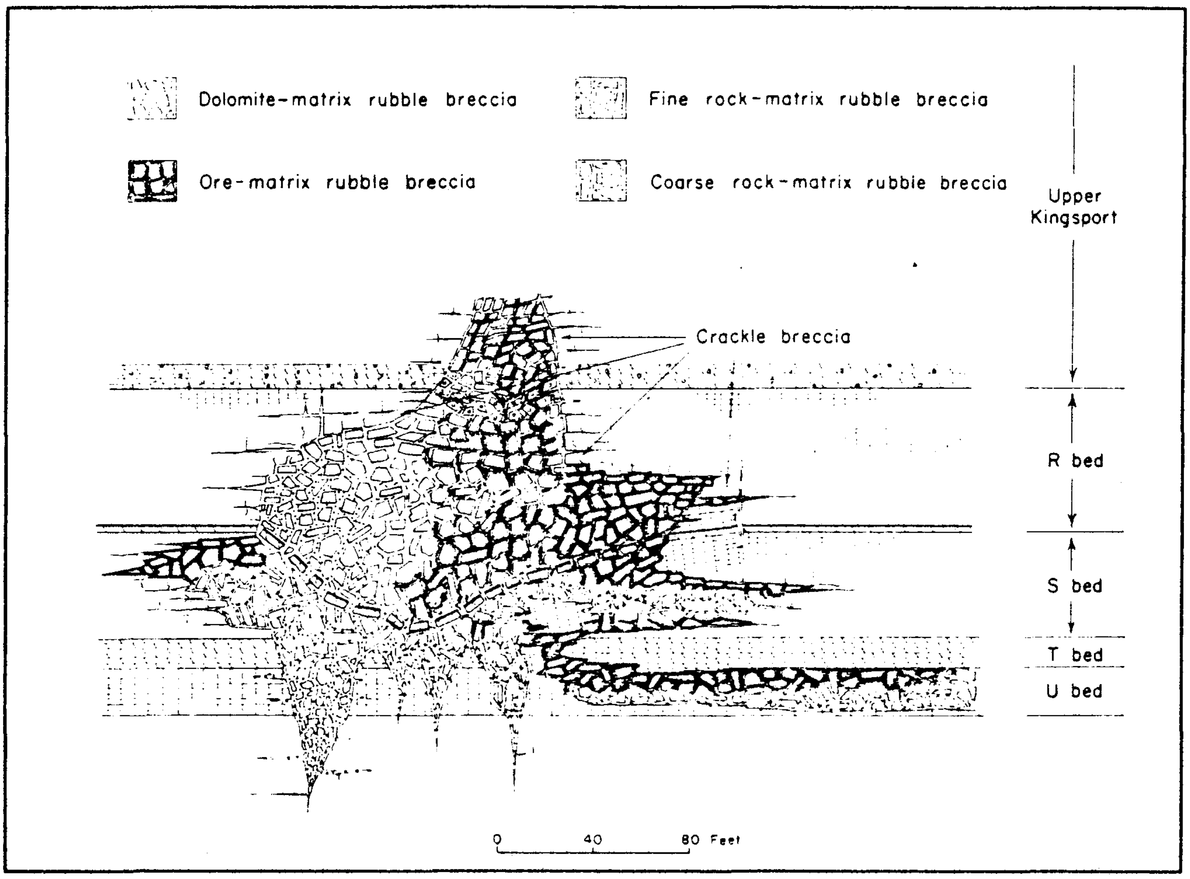


Detailed Stratigraphic Relationships of the Ore Beds of the Lower Kingsport and Upper Longview Formations (after Crawford)

Structural History

The principal ore controlling structures are the breccia zones; the majority of which are believed to have formed by dissolution of limestone beds and resulting collapse of the overlying dolomite beds. This occurred during a post-Lower Ordovician - pre-Middle Ordovician erosional interval that resulted in a regional karst System of underground drainage that extended to a depth of at least 800 feet. Brecciation occurs in all degrees from the crackle type in which the fragments have moved only slightly out of place to rubble breccias in which individual fragments have dropped as much as 50 feet and are rotated to all angles. These brecciated areas created extensive zones of subsurface permeability and circulation in the Kingsport formation. Mineralizing water responsible for dolomitization and zinc deposition found and made use of the permeable system and filled the open spaces with sphalerite and white dolomite. It is theorized that pre-ore structures controlled the localization of the great breccia zones. These structures of early Ordovician age were formed by processes of diagenesis involving dehydration and lithification of the sediments. This was followed by gentle folding and doming with resultant jointing. Minor flexures and folds developed, and areas of solution and collapse were localized there. When the immense breccia bodies were formed, these subtle structures were largely obliterated (Crawford and Hoagland, 1968).

Although the theories above are strongly held by many, evidence exists indicating that the presence and origin of ore and dolomite is not restricted to fracture filling processes, but may be hydrothermal



Generalized Section Through a Portion of the Jefferson City Mine in origin. Replacement textures of sphalerite in coarse grained crystalline dolomite rock are common. Typical ore bodies of the replacement type (some of which are the richest in the district), consist of masses of completely dolomitized limestone with abundant sphalerite and white coarse grained dolomite permeating the mass (Hill and Fulweiler, 1965).

As Kendall (1960) indicates, the brecciated areas may be tectonic in origin, and the ore deposits sedimentary, taking place at the time of deposition of the Kingsport formation. Small reef-like structures, possibly organic in origin, that are capped by layers of sphalerite are abundant in the brecciated dolomitized zones.

All three of these structural and genetical theories are filled with unexplained occurrences and controversy. The advocates of the highly developed karst system have yet to explain the fact that ground water generally does not have the capacity to create such a drainage system at the depths reported, e.g., 600-800 feet. Also, if the depositional agent was this same ground water one would expect less secondary dolomite and silica and more calcite.

Facts that seem difficult to explain by the hydrothermal theory are also abundant. One being the remarkable stratigraphic restriction of the ore. Another problem is the simple mineralogy of the district. And finally, drilling in the area has failed to locate any occurrence of inlets for these hydrothermal solutions.

The sedimentological theory fails to explain the abundance of ore in brecciated areas well above the Kingsport formation and across lithologic and faunal breaks and at local disconformity.

It is obvious that the origin of the brecciated and mineralized areas is complex and probably consists of a combination of two or all three of the listed theories. Further complicating the situation is the fact that the deposition of the ore took place prior to the Appalachian orogenic period. Appalachian structures of great intensity confused and largely obliterated the early structural situation.

Experimental Data

Thirteen uncovered and unpolished thin sections were made from five rock samples and were examined microscopically under plane polarized light, crossed nicols, and cathodoluminescence. Because the hand specimens and sections that were viewed without cathodoluminescence were basically identical in appearance and lithology, their descriptions will be condensed into a single section. A separate section is devoted entirely to the cathodoluminescent study.

Hand Specimen Description

Hand specimens could be considered to be of the rubble-type breccia described earlier. The host rock consists of a dark gray fine grained crystalline dolomite. The fracture filling material is a white coarsely crystalline dolomite with lesser quantities of sphalerite, pyrite and calcite. The coarsely crystalline white dolomite will be referred to as the gangue. In some cases the sphalerite can be found as a vuggy crust of well formed bright yellow crystals on the rock surface. In many of the fractures the dolomite gangue surrounds the sphalerite deposit and also may be found in the center of the mineral deposit. Assuming that the dolomite and sphalerite were deposited as open space filling deposits coating the rim of the fracture and filling inward, an important assumption can be made: The deposition of gangue dolomite started before the period of sphalerite mineralization and continued after the mineralization was completed.

The white dolomites that occur as bands or disseminations may differ in age and manner of formation, resulting either from deposition in open and porous spaces or from physical recrystallization. Some of the white filled fractures displace and offset one another. Some contain sphalerite and some do not. White mineralized fractures, in places, cut across both breccia fragments and the white gangue in the breccia matrix. In places the breccia matrix is composed of both white dolomite and dark gray coarse crystalline rock dolomite. The normal medium gray color becomes lighter or darker, the texture becomes coarser, and the rock is highly mottled by numerous irregular inclusions of white dolomite, which may represent recrystallization. Certain features resembling white fractures show gradation of the white dolomite into the country rock and also appear to represent recyrstallization.

Thin Section Study

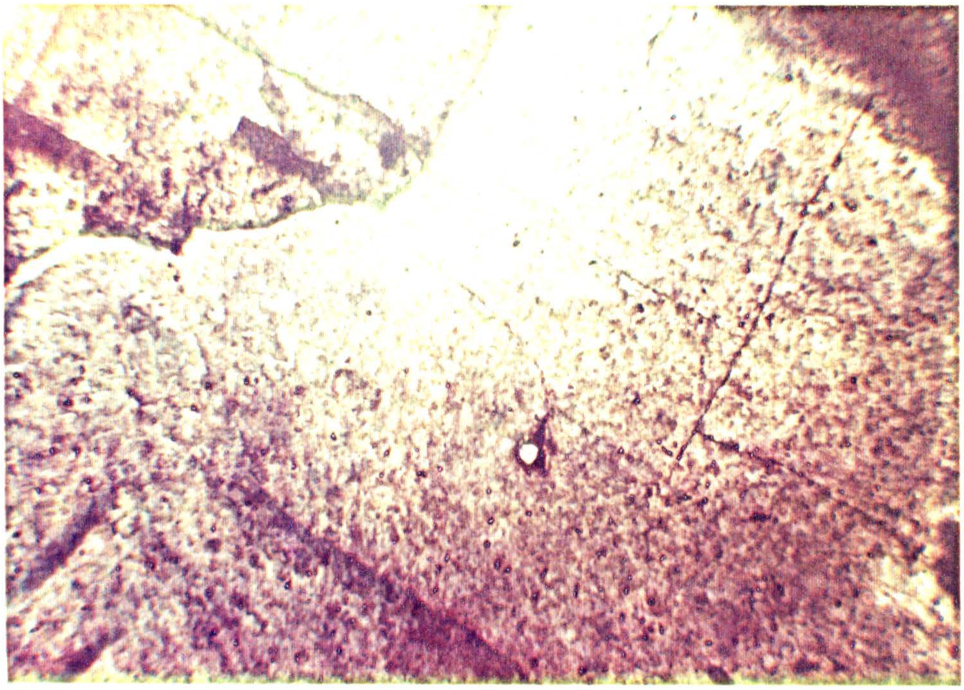
Due to the simplicity of the lithology of the rocks, the thin section evaluation with ordinary light and crossed nicols does not appreciably add data to that available in the hand specimens although it does reinforce the hand specimen data.

The rock is almost entirely dolomite (95%) in composition with minor sphalerite (5%) silica and pyrite (<1%). Fracturing along cleavage age angles can be seen in the host rock and in the gangue deposit. One thin section that was examined showed clastic layering of host rock, gangue, sphalerite, and small pockets of milky quartz indicating that fracturing and solution movement continued after the period of original deposition and some open spaces were filled with the sandy clastic material. Interruption of growth of gangue crystals by sphalerite, and sphalerite by gangue further supports the concept of deposition of gangue material both before and after mineralization. In many areas the boundary between white gangue and host rock is indistinct and seems to be gradational. Evidence exists to support both replacement and open-space filling in the region where the specimens were collected.

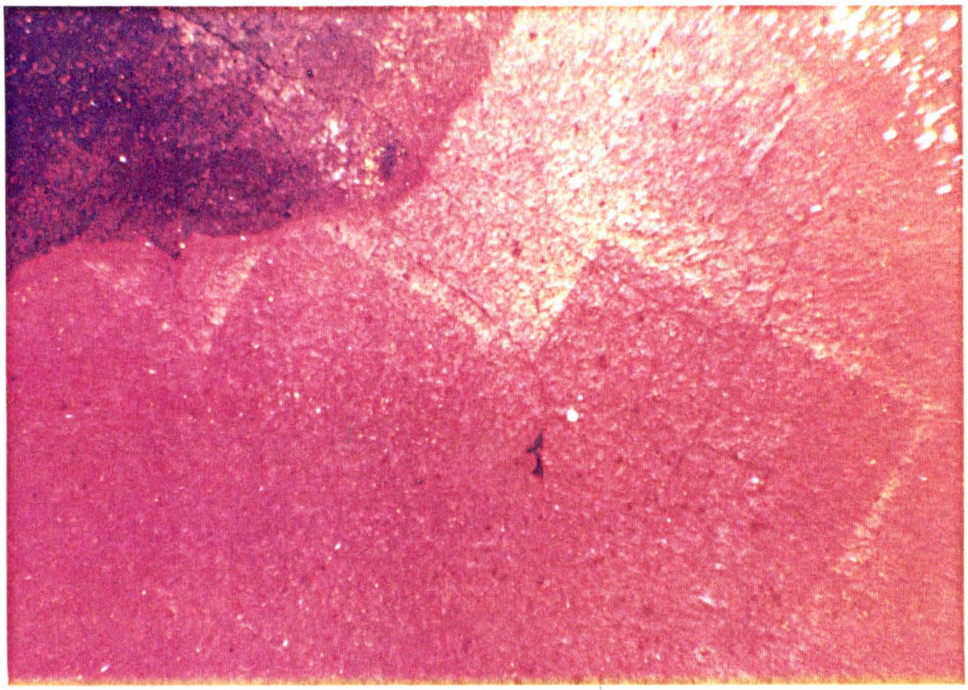
Cathodoluminescent Examination

When the thirteen thin sections were exposed to cathode rays, they fluoresced in the orange color characteristic of dolomite. This orange fluorescence is due to the presence of Mn^{+2}, which serves as a luminescent activator. Growth zones were observed in the gangue dolomite in five of the thirteen sections, all coming from the same rock sample. The zones are visible due to variations in luminescent color and intensity which are related to varying amounts of quenching elements such as iron, cobalt and nickel. In this case the quenching element is Fe^{+2}. If the Fe^{+2} content is too high (in the range .75 to 1.0 percent) the fluorescence may be quenched entirely (Mariano, 1978).

Photographic evidence, comparing the appearance of the sections in plane polarized light and under cathodoluminescence, make it clear that these sawtooth textured zones typical of an open-space filling are entirely invisible without luminescence (Figure 1a and 1b). The fractures seen in Figure 2a without luminescence appear as mere cleavage cracks. Under cathodoluminescence (Figure 2b) it is seen that the cracks are along the boundaries of separate growth zones. When zoning was seen, there was a definite trend in the relative thicknesses and

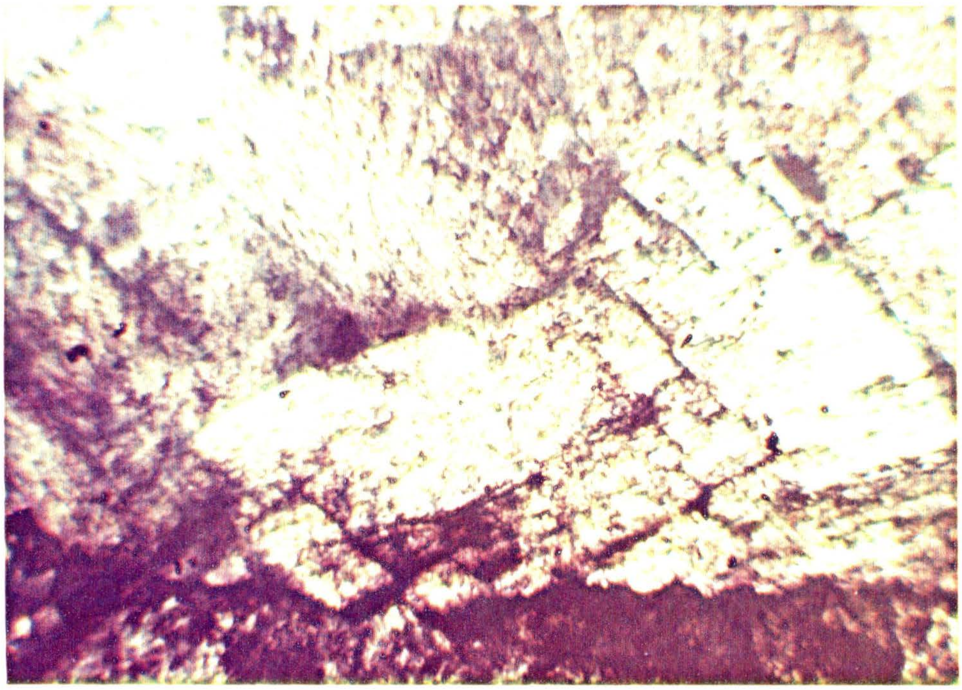


1a. Plane Polarized Light (10x)

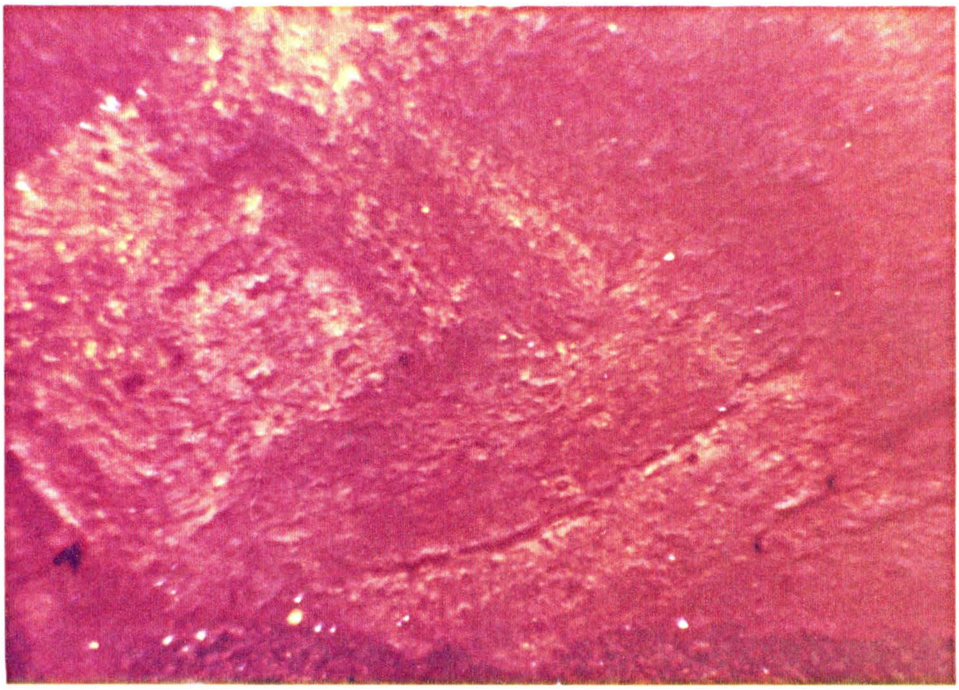


1b. Cathodoluminescence (10x) 35 mm Kodacolor 400 ASA

Figure 1.



2a. Plane Polarized Light (10x)



2b. Cathodoluminescence (10x) 35 mm Kodacolor 400 ASA

Figure 2.

color variations of the zones. From the rim of a fracture to its center, the series of zones encountered would be as follows: A relatively thick, bright zone; a series of relatively thinner and darker zones anywhere from one to four in number; and finally a thicker brighter zone. This sequence would then be repeated in reverse from the center of the fracture to opposite rim. The sequence generally was quite vague in the sections studied. In most cases, actual zone boundaries were not distinct, but the light-to-dark-to-light trend was apparent. Zoning was not noted in the remaining eight thin sections.

A Related Study

In 1979, Michael Ebers and Otto Kopp published a paper in Economic Geology entitled "Cathodoluminescent Microstratigraphy in gangue dolomite, the Mascot-Jefferson City District, Tennessee." In it they state:

> This study has shown that all the white gangue dolomite in the Mascot-Jefferson City District exhibits cathodoluminescent zonation associated with sphalerite mineralization which records its growth history as an open space filling. A total of six major zones were recognized which luminesce from very bright to very dark red. A nearly perfect microstratigraphic correlation of the gangue dolomite cathodoluminescent zones throughout the district was observed. A single period of sphalerite mineralization occurred during the development of three consecutive zones. The cathodoluminescent microstratigraphy reveals that both the sphalerite and gangue dolomite were time correlative through the Mascot-Jefferson City District.

These authors go on to say that:

> Correlation should only be attempted when two or more zones are present in an area where the zonal sequence is known. If possible, zones should be described from filled fractures where both sides of the fractures are visible. If the minerals in the fracture were deposited as an open space filling (and not by replacement), the zonal sequence should show a growth pattern from the edges of the fracture to the center. Zonal sequence determination is easier in a small filled fracture than in a complex rubble-breccia matrix.

Ebers and Kopp (1979) claimed to have solved the problem of location of ore in the Mascot-Jefferson City District. By looking for the three zones of dolomite, with which they claim the time of deposition of sphalerite can be correlated, one can decide whether or not an area will produce ore. Knowing the controversy over the structural picture of the region and also the many types of deposition proposed for the ore, the results of the study by Ebers and Kopp are hard to believe. A very simplistic picture of deposition, involving a series of uniform regional sweeps of mineralizing waters without the influences of any replacement or sedimentological processes, is needed for this theory to work. If in fact their findings are workable, and as they believe extendable into other mining districts, the implications are substantial.

Correlation Discussion and Conclusions

It was not possible to correlate the results of the cathodoluminescent study of the material from the Jefferson City mine to the work of Ebers and Kopp. As reported earlier, zoning was not prevalent in the white gangue dolomites of the Jefferson City mine. When it was detected, the zonal sequences, with respect to color and thickness, could not be correlated directly with those of the district-wide study. Ebers and Kopp indicate that the zoning record was difficult to ascertain in the complex matrix of the rubble breccia and the specimens used in the present study were primarily of this type. Interestingly, when a fracture was found in which both sides were visible no zoning was present.

Reasons for the discrepancies probably are related to the complicated and poorly understood nature of the brecciation and depositional history of the area. Evidence of recrystallization and replacement are abundant in the hand specimen descriptions. Although the majority of the gangue deposits are clearly open space filling, it seems that mineral alteration played an important role. Mineralizing (hydrothermal) waters may have washed through the partially or fully filled fractures and erased the zoning record within the gangue material.

A possible explanation for the differences in the zoning sequences of the present study and the study of Ebers and Kopp may be that within the Jefferson City mine brecciation and open spaces developed either before or after those of the other mines. This would mean that mineralizing waters had access to these fractures either prior to the rest of the district, or not until after the rest of the district was already mineralized.

A more detailed study should be carried out before concrete conclusions can be drawn concerning zoning in the Jefferson City mine. A larger number of samples from a wide range of depths within the mine may reveal data more in agreement with the results of Ebers and Kopp.

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